

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 375 469 A1

(12)

EUROPEAN PATENT APPLICATION

10/809,868

(43) Date of publication:
02.01.2004 Bulletin 2004/01

(51) Int Cl.7: C07C 51/58

(21) Application number: 03013110.6

(22) Date of filing: 11.06.2003

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR
Designated Extension States:
AL LT LV MK

(72) Inventors:
• Galimberti, Marco
20021 Bollate, Milano (IT)
• Navarrini, Walter
20010 Boffalora Ticino, Milano (IT)

(30) Priority: 21.06.2002 IT MI20021365

(74) Representative: Sama, Daniele, Dr. et al
Sama Patents,
Via G.B. Morgagni, 2
20129 Milano (IT)

(71) Applicant: Solvay Solexis S.p.A.
Milano (IT)

(54) A process for preparing acylfluorides

(57) A process for preparing acylfluorides by reaction of carbonyl fluoride COF_2 with compounds having general formula:



fluoroalkyl, optionally containing one or more oxygen atoms, t is an integer equal to zero or 1;

wherein a catalyst supported on porous compound is used, the catalyst being selected from: CsF, RbF, KF, AgF, each optionally in admixture with one or more of the others.

wherein:

- T is O or CF_2
- R_1 and R_2 , equal or different, are F or a $\text{R}(\text{O})_t$ radical, wherein R = linear or branched $\text{C}_1\text{-C}_7$ (per)

Description

[0001] The present invention relates to a process for obtaining acylfluorides with improved yields and selectivity.

[0002] Processes for obtaining acylfluorides are known in the prior art. In USP 3,113,967 it is described the acylfluoride synthesis by condensation between COF_2 and linear and cyclic fluoroolefins. The catalyst is selected from non oxidizing fluoride salts capable to make available the ion fluoride. Among cations, those of the elements of the first group are mentioned and, besides, iron, cobalt, nickel, zinc, tin, bismuth, tetraalkylammonium, trialkylammonium. In said patent it is mentioned that in the reaction the use of the solvent in combination with the metal fluoride is necessary to obtain high yields. In the Examples of said patent it is shown that in absence of solvent, the fluoroolefin being equal, the yields are lower. It is known that to obtain acylhalides it is necessary to operate in anhydrous environment. Therefore the used solvents must be treated to remove as much as possible the water traces. From an industrial point of view, the use of anhydrous solvents requires supplementary units and makes it harder to isolate the product from the reaction environment.

[0003] USP 3,114,778 describes the synthesis of perfluorinated vinyl ethers, wherein in the first step perfluorinated acylfluorides are reacted with hexafluoropropylene oxide (HFPO), in the presence of a catalyst formed by an alkaline metal fluoride, such for example CsF , in combination with an inert polar solvent. The reaction to obtain acylfluorides shows the same drawbacks mentioned above for the previous patent.

[0004] In USP 6,013,795 fluoroalkylcarbonyl compounds alpha branched to the carbonyl group are described. Said compounds, preferably having at least 8 carbon atoms, are synthesized by fluorination with F_2 , or by electrochemical route with HF in the presence of KF of the corresponding hydrogenated alkylcarbonyl compounds. In the patent it is mentioned that the yields for the electrochemical fluorination reaction are at most 50%, while for the direct fluorination reaction they are comprised between 60% and 80%. In this case there is however the drawback of a high fluorine consumption, which as known is an expensive reactant and is to be cautiously used. Besides it is known that both the above processes lead to the formation of various by-products making them not optimal from the industrial point of view.

[0005] The need was felt to have available a process for obtaining by direct synthesis, also starting from (per) fluoroolefins, acylfluorides with improved yields and selectivity, even by continuously operating.

[0006] The Applicant has surprisingly and unexpectedly found that by using the process described herein after it is possible to solve the above technical problem, and therefore to have available a simplified industrial process capable to operate even continuously, through

which it is possible to obtain acylfluorides with improved yields and selectivity.

[0007] An object of the present invention is a process for preparing acylfluorides by reaction of

carbonyl fluoride (COF_2)

with compounds having general formula:



wherein:

- T is O or CF_2
- R_1 and R_2 , equal or different, are F or a $\text{R}(\text{O})_t$ radical, with the proviso that:

- when $\text{T} = \text{CF}_2$, then:

$\text{R} =$ linear or branched $\text{C}_1\text{-C}_7$ (per) fluoroalkyl, preferably $\text{C}_1\text{-C}_5$, optionally containing one or more oxygen atoms,
t is an integer equal to zero or 1;

- when T is oxygen, then:

R_1 and R_2 are equal to each other and have the meaning of $\text{R} = \text{C}_1\text{-C}_7$ (per) fluoroalkyl, optionally containing one or more oxygen atoms, with $t = 0$;

wherein a catalyst supported on porous compound is used, the catalyst being selected from:

- CsF , RbF , KF , AgF , each optionally in admixture with one or more of the others,

wherein the porous compound is formed by a compound inert under the reaction conditions and has a porosity, determined by the mercury-helium method, and expressed as ratio between the pore volume and the total solid volume, higher than 0.2, preferably higher than 0.3.

[0008] The formula (I) compounds are known compounds.

[0009] The ratio by moles between COF_2 and the formula (I) compounds ranges from 1:1 to 6:1.

[0010] Preferably the porous compound which forms the catalyst support is constituted by one or more fluorides selected from one or more of the following groups:

- alkaline metal fluorides, preferably LiF and NaF ;
- alkaline-earth metal fluorides, preferably the following: CaF_2 , BaF_2 , MgF_2 , SrF_2 ;
- AgF .

[0011] When the porous support is formed by one or more fluorides indicated as catalysts, the porous support forms the catalyst. On the porous support one or

more of the above mentioned catalysts can be supported.

[0012] The condensation reaction between the compounds of formula (I) and COF_2 according to the present invention is carried out at a temperature in the range 100°C - 400°C , preferably 150°C - 300°C .

[0013] Preferably the reaction is carried out in gaseous phase.

[0014] The conversion of the formula (I) compound in the process according to the present invention is generally very high, even higher than 90% and the selectivity always remains very high, even when the conversion of the formula (I) compound is not complete.

[0015] An advantage of the process according to the present invention is that by starting from (per)fluoroolefins of formula (I) the main by-product is a (per)fluoroketone; when the (per) fluoroketone is among the compounds defined in formula (I) with $T = \text{oxygen}$, it can be used in the reaction according to the present invention and therefore it is possible to increase the total yields in acylfluoride. See the Examples.

[0016] The process of the present invention can be carried out in a continuous way or in batch.

[0017] The pressure at which one operates is generally that atmospheric and it is anyway possible to operate also at higher pressures, for example up to 40 Atm ($4.05 \cdot 10^6$ Pa).

[0018] When compounds of formula (I) having boiling point higher than or equal to the room temperature are used, it is possible to dilute the reactants with an inert gas, for example nitrogen, helium.

[0019] In this case it is possible to use as diluent, alternatively to the above described inert gases, also an inert perfluorocarbon or a perfluoroether, at the vapour state under the reaction conditions, such for example C_3F_8 , C_2F_6 , cyclo- C_4F_8 , C_4F_{10} .

[0020] The contact times in the continuous process are comprised between 2 seconds and 1 minute, depending on the reactor shape and the reactant flows.

[0021] When the porous support is formed by one or more fluorides selected from the above groups, it is preferably obtainable starting from the corresponding acid fluorides and heating at a temperature in the range 450°C - 550°C in an inert gas flow, so to obtain the substantial removal of the hydrofluoric acid.

[0022] The catalyst is deposited on the porous support by impregnating the latter with a solution containing dissolved the metal fluoride catalyst and removing the solvent by heating in inert gas flow or by evaporation at reduced pressure. The solvent must not solubilize the porous support. Preferably the solutions containing the catalyst are based on alcohols, preferably methanol. Mixtures of alcohols with other solvents can be used with the proviso that they do not solubilize the porous support.

[0023] The skilled man in the field is capable to prepare said mixtures knowing the metal fluoride used to prepare the support and that to be used as catalyst.

[0024] The concentration by weight of the metal fluoride as catalyst which is supported can range from 1% up to 40% by weight and more, preferably from 10 to 30% by weight.

[0025] The preferred supported catalyst uses as catalyst CsF and as a support NaF .

[0026] The catalyst has a particle size suitable for a fixed or a fluidized bed. In the case of a fixed bed generally the minimum particle size must not be lower than 0.05 mm. The feasible sizes depend on the catalyst support compound shape, for example, spheres, cylinders or granules.

[0027] As said, the present invention catalyst is used in the reactions between the formula (I) compounds, preferably (per) fluoroolefins, and COF_2 .

[0028] As said, the acylfluoride reaction products are obtained with improved yields and selectivity.

[0029] With the term "yield" it is meant the ratio (expressed in percentage) between the obtained acylfluorides moles and the theoretically obtainable moles according to the reaction stoichiometry in the case of complete conversion to acylfluoride of the limiting reactant.

[0030] With the term "selectivity" it is meant the ratio (expressed in percentage) between the obtained acylfluoride moles and those theoretically obtainable, according to the reaction stoichiometry, calculated on the reactant moles really converted during the reaction.

[0031] The catalyst activity is maintained for long periods, for example even over one year, and ratios between the converted moles of the formula (I) compound and the catalyst moles higher than 100, are reached.

[0032] A further process advantage according to the present invention is that one can operate in absence of solvent.

[0033] If desired, one can operate in the presence of a dipolar aprotic solvent, for example mono- or polyglyme, acetonitrile, DMF.

[0034] In this case the invention process can be carried out even at lower temperatures. Generally the solvent amounts are equal to or lower than the weight of the used supported catalyst.

[0035] The acylfluorides obtainable by the invention process have the following general formula:



wherein:

$\text{R}^1 = \text{CF}_3\text{R}_1\text{R}_2\text{C}$ wherein R_1 and R_2 are as defined in the formula (I) compound when $T = \text{CF}_2$, or $\text{R}^1 = \text{R}_1 = \text{R}_2$ as above defined in the formula (I) compound when T is oxygen.

[0036] The following Examples illustrate the invention without limiting the scope thereof.

EXAMPLES

EXAMPLE 1

Catalyst preparation

[0037] 25 g of NaHF_2 sodium acid fluoride are slowly heated in a nitrogen flow of 2 litres/h up to the temperature of 500°C , and maintained under these conditions for about one hour, until HF results almost completely removed from the support. 16 g of NaF with a porosity equal to 0.40 are obtained. The support is then charged in a rotating evaporator and degassed under vacuum at room temperature. Then a solution of 5 g of CsF dissolved in 10 cc of methyl alcohol is then sucked in the evaporator to impregnate the support and then drying under vacuum is continued at the temperature of 80°C to 90°C .

[0038] The so prepared catalyst is introduced into the used reactor and dried in an inert gas flow at the temperature of 200°C to 250°C for two hours before being used. The catalyst porosity is 0.38.

EXAMPLE 2

Synthesis in a continuous way of perfluoroisobutyryl fluoride $(\text{CF}_3)_2\text{CFCOF}$

[0039] 434 g of CsF catalyst supported on NaF prepared as described in the Example 1 are introduced in a 270 cm^3 tubular reactor having the diameter of 2.5 cm. They are then activated by heating at 200°C in He flow. Such catalyst is then saturated with a COF_2 flow at the temperature of 190°C .

[0040] The acylfluoride synthesis is carried out by flowing on the catalytic bed a flow of 2.0 litres/h (l/h) of COF_2 (obtained by direct reaction between 2.0 l/h of CO and 2.1 l/h of F_2) and 1.75 litres/h of perfluoropropene C_3F_6 . The reaction progress is followed by analyzing by GC and IR analyses the gases flowing out from the reactor; once the balance is reached, the product is conveyed to a storing bottle maintained at -196°C . After distillation in vacuum ramp at 10^{-3} mbar (0.1 Pa), the acylfluoride is recovered with a yield and selectivity of 95%.

EXAMPLE 3

Synthesis in a continuous way of perfluoro-2 methoxypropionyl fluoride $(\text{CF}_3)(\text{CF}_3\text{O})\text{CFCOF}$

[0041] The same reactor used in the Example 2, containing the same activated catalyst, is washed with a COF_2 flow at the temperature of 210°C .

[0042] The acylfluoride synthesis is carried out by flowing on the catalytic bed, maintained at 210°C , a flow of 2.0 l/h of COF_2 (obtained by direct reaction between 2.2 l/h of CO and 2.0 l/h of F_2) and 1.25 l/h of perfluoro-

methylvinylether $\text{CF}_2=\text{CR}-\text{O}-\text{CF}_3$. The reaction progress is followed by analyzing by GC and IR analyses the gases flowing out from the reactor; once the balance is reached, the product is conveyed to a storing bottle maintained at -196°C . After distillation in vacuum ramp at 10^{-3} mbar, the acylfluoride is recovered with a yield and selectivity of 93%.

Characterization $(\text{CF}_3)(\text{CF}_3\text{O})\text{CFCOF}$

[0043]

- Boiling point at atmospheric pressure: 10°C . Experimental curve of the vapour tension (P in mbar and T in K): $\ln(P)=19.697-3620.4/T$.
- ^{19}F NMR spectrum in ppm ($\text{CFCl}_3=0$): 26.7 (1F, $-\text{COF}$); -56.5 (3F, $-\text{OCF}_3$); -82.4 (3F, $-\text{CF}_3$); -132.7 (1F, CF).
- Mass spectrum (electronic impact): main peaks and relative intensities: 31(25), 47(30), 69(100), 98(47), 119(78), 147(9), 185(25).
- IR spectrum (cm^{-1}) (intensity: w = weak, m = mean, s = strong, vs = very strong): 1888 (s), 1338 (w), 1294 (vs), 1248 (vs), 1159 (vs), 1225 (s), 1015(s), 899(w), 699 (w).

EXAMPLE 4

Synthesis in a continuous way of perfluoropropionyl fluoride $\text{CF}_3\text{CF}_2\text{COF}$

[0044] The same reactor used in the Example 3, containing the activated catalyst of Example 2, is washed with a COF_2 flow at the temperature of 250°C .

[0045] The acylfluoride synthesis is carried out by flowing on the catalytic bed, maintained at 250°C , a flow of 2.0 l/h of COF_2 (obtained by direct reaction between 2.2 l/h of CO and 2.0 l/h of F_2) and 1.0 l/h of tetrafluoroethylene inhibited with β -terpene. The reaction progress is followed by analyzing by GC and IR analyses the gases flowing out from the reactor; once the balance is reached, the product is conveyed to a storing bottle maintained at -196°C . After distillation in vacuum ramp at 10^{-3} mbar (0.1 Pa), the acylfluoride is recovered with a yield and selectivity of 68%. The main by-product is the $\text{C}_2\text{F}_5\text{COC}_2\text{F}_5$ ketone.

EXAMPLE 5

Synthesis in batch of perfluoro-2,2-dimethoxypropionyl fluoride $(\text{CF}_3)(\text{CF}_3\text{O})_2\text{CCOF}$

[0046] 240 mmoles of COF_2 and 192 mmoles of perfluoro-1,1-dimethoxyethylene $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$ are condensed in a 325 ml reactor equipped with manometer, containing 30 g of supported catalyst prepared as described in the Example 1, activated by heating at 200°C

under vacuum at 10^{-3} mbar (0.1 Pa) for 2 hours. The whole is heated at 190°C for 40 hours and then at 200°C for 43 hours, until the internal pressure stabilizes. At this point the reaction does not further proceed and then one proceeds to recover the product by successive distillations in vacuum ramp at 10^{-3} mbar (0.1 Pa) through three traps, cooled respectively at -65°C , -110°C and -196°C . The acylfluoride $(\text{CF}_3)_2\text{CFCOF}$ is isolated in the trap at -65°C with a 60% yield and a 78% selectivity. The other component of the reacted mixture is the starting olefin.

Characterization $(\text{CF}_3)_2\text{CFCOF}$

[0047]

- Boiling point at atmospheric pressure: 41°C .
- Experimental curve of the vapour tension (P in mbar and T in K): $\ln(P) = 18.928 - 3769.6/T$.
- ^{19}F NMR spectrum in ppm ($\text{CFCl}_3=0$):
26 (1F, -COF); -59.6 (6F, -OCF₃); -81.8 (3F, -CF₃).
- Mass spectrum (electronic impact): main peaks and relative intensities:
47(3), 69(100), 97(6), 167(2), 232(2), 251(1).
- IR spectrum (cm^{-1}) (intensity: w = weak, m = mean, s = strong, vs = very strong):
1885(s), 1292(vs), 1258(vs), 1159(m), 1227 (s), 1015 (m), 890 (w).

EXAMPLE 6

Synthesis in batch of perfluoroisobutyl fluoride $(\text{CF}_3)_2\text{CFCOF}$ by retrocondensation of perfluoro(bis-isobutyl)ketone $(\text{CF}_3)_2\text{CFCOCF}(\text{CF}_3)_2$

[0048] The same reactor of Example 5 is used for this reaction; the catalyst, CsF supported on NaF (Example 1), is activated by heating at 200°C under vacuum at 10^{-3} mbar (10^{-2} Pa) for 4 hours. 59 mmoles of COF_2 and 12 mmoles of $(\text{CF}_3)_2\text{CFCOCF}(\text{CF}_3)_2$ are then condensed. It is heated at 250°C for 5 hours and then one proceeds to recover the product by successive distillations in vacuum ramp at 10^{-3} mbar through three traps cooled respectively at -50°C , -110°C and -196°C .

[0049] 23.6 mmoles of acylfluoride $(\text{CF}_3)_2\text{CFCOF}$ are isolated in the trap at -110°C with a yield and selectivity of 98%.

EXAMPLE 7 (comparative)

Synthesis of $(\text{CF}_3)_2\text{CFCOF}$ in a continuous way using as catalyst unsupported CsF

[0050] 87 g of CsF in powder are introduced into a tubular reactor equal to that of the Example 2. They are then activated as described in the Example 2.

[0051] By repeating the reaction on perfluoropropene as described in the Example 2, by gaschromatographic

analysis it is found that the perfluoropropene conversion to acylfluoride is of 15%.

EXAMPLE 8

Synthesis of $(\text{CF}_3)_2\text{CFCOF}$ in batch using as catalyst supported CsF

[0052] 7.74 g of supported catalyst (corresponding to 10 mmoles of CsF) which are activated by heating at 300°C under vacuum (10^{-3} mbar) for three hours are introduced into a 150 ml autoclave equipped with pressure transducer. Then 60 mmoles of perfluoropropene and 80 mmoles of COF_2 are condensed in the autoclave. The system is heated at the reaction temperature of 190°C . The pressure reduction is followed in the time.
[0053] After 14 hours the heating is turned off and the autoclave content is transferred into a vacuum ramp.
[0054] By distillation under vacuum at 10^{-3} mbar (10^{-2} Pa) the acylfluoride $(\text{CF}_3)_2\text{CFCOF}$ is recovered. The yield is 77% and the selectivity is 81%. The main reaction by-product is the $\text{C}_3\text{F}_7\text{COC}_3\text{F}_7$ ketone (yield 10%).

EXAMPLE 9 (comparative)

Synthesis of $(\text{CF}_3)_2\text{CFCOF}$ in batch by using as catalyst unsupported CsF

[0055] Example 8 is repeated using CsF in powder at the place of the supported catalyst, in the same amount (10 mmoles). The yield of $(\text{CF}_3)_2\text{CFCOF}$ is 10%.

Claims

1. A process for preparing acylfluorides by reaction of carbonyl fluoride COF_2 with compounds having general formula:



wherein:

- T is O or CF_2
- R_1 and R_2 , equal or different, are F or a $\text{R}(\text{O})_t$ radical, with the proviso that:

- when $\text{T} = \text{CF}_2$, then:

R = linear or branched $\text{C}_1\text{-C}_7$ (per) fluoroalkyl, preferably $\text{C}_1\text{-C}_5$, optionally containing one or more oxygen atoms,
t is an integer equal to zero or 1;

- when T is oxygen, then:

R_1 and R_2 are equal to each other and have the meaning of $R = C_1-C_7$ (per) fluoroalkyl, optionally containing one or more oxygen atoms, with $t = 0$;

wherein a catalyst supported on porous compound is used, the catalyst being selected from:

- CsF, RbF, KF, AgF, each optionally in admixture with one or more of the others,

wherein the porous compound is formed by a compound inert under the reaction conditions and has a porosity, determined by the mercury-helium method, and expressed as ratio between the pore volume and the total solid volume, higher than 0.2, preferably higher than 0.3.

2. A process according to claim 1, wherein the ratio by moles between COF_2 and the formula (I) compounds ranges from 1:1 to 6:1. 20
3. A process according to claims 1-2, wherein the porous compound which forms the catalyst support is constituted by one or more fluorides selected from one or more of the following groups: 25
 - alkaline metal fluorides, preferably LiF and NaF; 30
 - alkaline-earth metal fluorides, preferably the following: CaF_2 , BaF_2 , MgF_2 , SrF_2 ;
 - AgF. 30
4. A process according to claims 1-3, wherein when the porous support is constituted by one or more fluorides indicated as catalysts, the porous support constitutes the catalyst. 35
5. A process according to claims 1-4, wherein the temperature is in the range $100^\circ C-400^\circ C$, preferably $150^\circ C-300^\circ C$. 40
6. A process according to claims 1-5 carried out in gaseous phase. 45
7. A process according to claims 1-6 carried out in a continuous way or in batch.
8. A process according to claims 1-7, wherein the used pressure ranges from the atmospheric pressure to 40 Atm ($4.05 \cdot 10^6$ Pa). 50
9. A process according to claims 1-8, wherein inert gases are used as diluents, preferably nitrogen or helium, or perfluorocarbons or perfluoroethers, preferably C_3F_8 , C_2F_6 , cyclo- C_4F_8 , C_4F_{10} . 55
10. A process according to claims 7-9 continuously carried out wherein the contact times are comprised between 2 seconds and 1 minute.
11. A process according to claims 1-10, wherein the concentration by weight of the metal fluoride catalyst which is supported ranges from 1% up to 40% by weight, preferably from 10 to 30% by weight. 5
12. A process according to claims 1-11, wherein the catalyst is CsF supported on NaF. 10
13. A process according to claims 1-12, wherein one operates in the presence of a dipolar aprotic solvent, in an amount by weight equal to or lower than the weight of the used catalyst. 15



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 03 01 3110

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| D,A | US 3 113 967 A (FAWCETT FRANK S) 10 December 1963 (1963-12-10) * the whole document * | 1 | C07C51/58 |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.7) |
| | | | C07C |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 23 September 2003 | Examiner Delanghe, P |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | |

EPO FORM 1501 03.02 (P/N/C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 03 01 3110

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-09-2003

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US 3113967 | A | 10-12-1963 | NONE |
| <div data-bbox="794 810 1213 1043" data-label="Text"><p>SAMA PATENTS</p><p>14 GEN. 2004</p><p>RECEIVED</p></div> <p data-bbox="803 1077 1344 1192"><i>same g.e. schedule SP(S) : 02.07.04</i></p> <p data-bbox="1187 1276 1425 1339"><i>copy OK</i></p> | | | |

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82